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ALKALI-RESISTANT MINERAL FIBRES – A REVIEW

S.S.B. WANG

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ALKALI-RESISTANT MINERAL FIBRES - A REVIEW

by

S.S.B. Wang*

ABSTRACT

This literature review presents background information outlining the function of mineral fibres in cement and concrete mixes. Asbestos fibres are currently used because of their alkali-resistant properties. Newly developed alkali-resistant man-made mineral fibres (MMMF) have been developed as possible substitutes. Problems relative to such fibres are noted along with the desirability of researching alternate fibre-forming mineral materials, e.g., asbestos tailings and diopside.

The various types and grades of mineral wool and typical raw mineral materials are identified and reviewed as are the major mineral wool-forming processes, furnaces and fiberization methods. Glass fibre properties and fundamental considerations of the nature of glass and glass fibre are then reviewed following which the mechanics of chemical attack on glasses in aqueous solutions is considered. Finally, alkali-resistant fibres are reviewed and alkali-resistant evaluation tests described.

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FIBRES RÉSISTANTES AUX ALCALIS: ÉTUDE DOCUMENTAIRE

par

S.S.B. Wang*

RÉSUMÉ

Cette étude documentaire présente les données de base sur le rôle des fibres minérales dans les mélanges de ciment et béton. Actuellement, on utilise les fibres d'amiante en raison de leur résistance aux alcalis, mais des fibres minérales synthétiques résistantes aux alcalis ont été mises au point comme des substituts possibles. On tire l'attention sur les problèmes relatifs à de telles fibres et sur les avantages de faire de la recherche sur d'autres matériaux minéraux pouvant être transformés en fibres, comme les résidus d'amiante et le diopside.

On identifie et réexamine les divers types et qualités de laine minérale ainsi que les matières minérales premières et les principaux procédés de fabrication de la laine minérale, les fours et les méthodes de transformation en fibres. Ensuite, on réexamine les propriétés de la fibre de verre et les considérations fondamentales concernant la nature du verre et sa fibre ainsi que les mécanismes de l'attaque chimique de verres en solutions aqueuses. Finalement, on passe en revue les fibres résistantes aux alcalis et les essais d'évaluation de résistance aux alcalis.

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INTRODUCTION

Cement and concrete products have high compressive strengths but are very weak in tension and lack toughness. To overcome these shortcomings they have to be reinforced. Concrete is strengthened conventionally using steel rods, and cement using asbestos fibres.

Asbestos cement, in which a firm bond is formed between fibre and cement, is strong, durable, rigid and resistant to freezing and thawing, humidity and fire. It has sufficient wet strength to allow molding into flat or corrugated sheets, pipe and a variety of other shapes. However, because of potential health risks, an attempt is being made to replace asbestos by other materials such as glass and organic fibres. The major requirements of a suitable fibre for reinforcement are high strength and elastic modulus, a reasonable bond at the interface, and good chemical stability. Organic natural and synthetic fibres have a high residual elongation and are poor in tensile strength and elasticity. Also, they do not bond well with cement matrix. The large difference in specific gravity between the fibres and cement causes a segregation problem in the mixture. Conversely, glass fibres have reasonably high tensile strength, wear resistance, stiffness, and hardness. They have a low elongation and therefore ensure high dimensional stability. Glass fibres and cement mortar have comparative specific gravities. Cement-based matrices have very strong alkalinity (pH ≈12.5). Glass fibres made from soda-lime-silica or borosilicate compositions, which were tried as reinforcement, were corroded by the highly alkaline cement paste and lost their strengthening power quickly. Alkali-resistant fibres having high zirconia content (16-17%) were developed and are now commercially available under the name "Cem-Fil". The alkaline durability of Cem-Fil fibres in the short term appears satisfactory, but the long-term performance is unconfirmed. The product also has two main disadvantages: zirconia is costly, and its addition to silicate increases the melting and fiberizing temperatures, thereby increasing production costs (1). Cem-Fil fibres cost U.S. $4700/t compared with U.S. $1000/t for asbestos fibres. In view of this, CANMET initiated a project to develop alkali-resistant fibre compositions from inexpensive and more readily available raw materials such as diopside and asbestos tailings. This literature review is the first part of the ongoing project.

MINERAL WOOL

"Mineral wool" is a generic term covering a large group of fibrous products made from different mineral materials. These products are manufactured mainly for thermal insulation and can be generally classified by the composition of the original furnace charge (2):

(a) glass wool which is formed chiefly from mixtures of sand, soda ash, limestone, feldspar, barytes and, in some cases, scrap glass;

(b) slag wool which is formed from iron, copper or lead furnace slags and fluxing or melt composition adjusting materials such as sandstone;

(c) rock wool which is formed from naturally occurring rocks.

The mineral wool manufacturing process essentially consists of two steps: melting the charge materials and fiberizing the melt.

Raw Material Selection

Common glass fibres can be divided into two main groups: soda-lime-silica and borosilicate. Typical compositions are shown in Table 1.

Table 1 - Typical compositions of three different glasses (2)

%	Soda-lime-silica glass	Borosilicate glass "E"	Glass fibre "C"
Silica	72.2	53.3	62-65
Lime	9.5	17.5	6
Magnesia	3.5	4.5	-
Alumina	1.8	14.5	1
Soda	13.0	-	11-15
Potash	-	-	1-3
Boric oxide	-	10.0	3-4

Table 2 - Principal raw materials for glass making (8)

Material	Alternative name	Theoretical formula	Oxides supplied	Fraction
Alumina	Calcined alumina	Al_2O_3	Al_2O_3	1.00
Alumina hydrate	Hydrated alumina	$Al_2O_3.3H_2O$	Al_2O_3	0.654
Aplite (typical	-	-	Al_2O_3	0.240
composition)	-	-	$Na_2(K_2)O$	0.100
	-	-	SiO_2	0.600
	-	-	CaO	0.060
Feldspar	Microline (com-	$K_2O.Al_2O_3.6SiO_2$	Al_2O_3	0.180
	position is of	-	$K_2(Na_2)O$	0.130
	typical com-	-	SiO_2	0.680
	mercial spar)			
Nepheline syenite	-	-	Al_2O_3	0.250
(typical com-	-	-	$Na_2(K_2)O$	0.150
position)	-	-	SiO_2	0.600
Calumite	Calcium-aluminum	$2CaO.MgO.2SiO_2$	SiO_2	0.380
	silicate	$2CaO.Al_2O_3.SiO_2$	Al_2O_3	0.117
		$2(CaO.SiO_2)$	CaO	0.400
			MgO	0.080
Kyanite (90%	-	$Al_2O_3.SiO_2$	Al_2O_3	0.567
concentrate)	-	-	SiO_2	0.433
Kaolin	China clay	$Al_2O_3.2SiO_2.2H_2O$	Al_2O_3	0.395
	-	-	SiO_2	0.465
Cryolite	Kryolith	Na_3AlF_6	-	---
Antimony oxide	-	Sb_2O_3	Sb_2O_3	1.000
Barium carbonate	-	$BaCO_3$	BaO	0.777
Barium oxide	Baryta	BaO	BaO	1.000
Barium sulphate	Barytes	$BaSO_4$	BaO	0.657
Boric acid	Boracic acid	$B_2O_3.3H_2O$	B_2O_3	0.563
Borax	-	$Na_2O.2B_2O_3.10H_2O$	B_2O_3	0.365
	-	-	Na_2O	0.163
Anhydrous borax	("Pyrobor")	$Na_2O.2B_2O_3$	B_2O_3	0.692
	-	-	Na_2O	0.308
Lime, burnt	Quick lime	CaO	CaO	1.000
Lime, hydrated	Calcium hydrate	$CaO.H_2O$	CaO	0.757
Limestone	Calcium carbonate	$CaCO_3$	CaO	0.560
Calcium carbonate	Whiting	$CaCO_3$	CaO	0.560
Lime, dolomitic	Burnt dolomite	CaO.MgO	CaO	0.582
	-	-	MgO	0.418
Dolomite	Raw limestone	$CaO.MgO.2CO_2$	CaO	0.304
	(dolomitic)	-	MgO	0.218
Lime, hydrated,	Finishing lime	$CaO.MgO.2H_2O$	CaO	0.423
dolomitic	-		MgO	0.304
Bone ash	Calcium	$3CaO.2P_2O_5+$	CaO	0.372
	phosphate	$XCaCO_3$	P_2O_5	0.628
Potassium carbon-	Calcined carbon-	K_2CO_3	K_2O	0.681
ate	ate of potash			
Glassmaker's	Potassium	$K_2CO_3.1.5H_2O$	K_2O	0.570
potash	carbonate, hyd.			
Sand	Glass sand,	SiO_2	SiO_2	1.000
	quartz			
Soda ash	Sodium carbonate	Na_2CO_3	Na_2O	0.585
Salt cake	Sodium sulphate	Na_2SO_4	Na_2O	0.437
Sodium	Sodium	Na_2SiF_6	-	-
silicofluoride	fluosilicate			
Zinc oxide	-	ZnO	ZnO	1.000

Water leaches soda from the body of soda-lime-silica glass which greatly reduces the fibre strength. The borosilicate glass is alkali-free and consequently resistant to water and weathering. A glass fibre "C" was also developed, which has high resistance to alkalis and acids, and is used in chemical applications such as filter cloth and anode bags (2).

Silica (SiO_2) is the principal glass-forming oxide. It is used as sand or, in lump form, as sandstone. The second common ingredients are alkalis (Na_2O and K_2O) which are added to lower the melting temperature of the glass batch and shorten the refining time; however, too high an alkali content in the glass fibres tends to decrease fibre strength and to increase their susceptibility to water attack. The third ingredient is lime (CaO). Calcium and magnesium oxide have a stabilizing influence when alkali-lime-silica glasses are attacked by water. Alumina is added to improve the durability and resistance to weathering and to reduce devitrification (2). Boric oxide (B_2O_3) is used for fluxing. Progressive additions of boric oxide significantly increase the melting rate of soda-lime-silica glass. Increase of B_2O_3 from 0 to 2.5% lowers the viscosity from 1400°C to a point between 602 and 625°C, depending on the basic composition, below which the introduction of B_2O_3 progressively increases viscosity (3).

Some of the principal raw materials and oxides for glass making are listed in Table 2.

Table 3 - Chemical compositions of raw materials for rock and slag wool production

%	Argillaceous dolomite	Sandstone	Blast furnace slag
SiO_2	24.3	88.5	38.0
Al_2O_3	11.2	1.1	8.2
Fe_2O_3	0.8	2.2	0.6
CaO	21.5	5.2	38.0
MgO	11.2	-	19.0
LOI*	29.1	3.1	-

*LOI - loss on ignition

Rock wool is made from natural rocks or minerals such as self-fluxing argillaceous dolomite. Slag wool is produced mainly from iron blast furnace slag with the addition of lime or silica-bearing materials, e.g., sandstone used as flux and to adjust the melt viscosity. Typical chemical compositions of raw materials for rock and slag wool production are given in Table 3.

Melting Furnaces

Conventional gas or electric melting furnaces for glass making are generally used for glass wool production, but the majority of slag wool and rock wool producers use cupolas (Fig. 1).

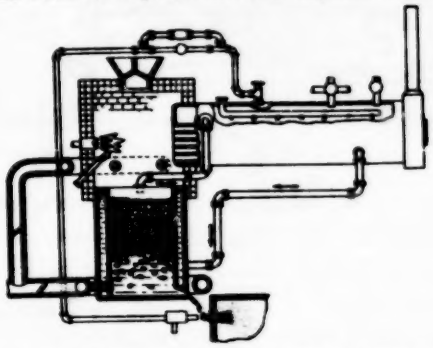


Fig. 1 - Steel-jacketed water cooled cupola furnace (2).

The cupola is usually water-cooled and not lined with refractory material. It is filled with alternate layers of fuel (coke) and raw materials up to the charging door. The materials have to be in lump form to allow free passage of air and combustion gases and to reduce material loss up the stack. Reverberatory furnaces fired with oil or gas are also used. Reverberatory and electric furnaces allow the use of fine raw materials, thus recycling of waste shot is feasible (Fig. 2, 3).

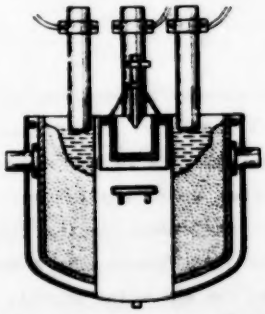


Fig. 2 - Electric arc furnace (2).

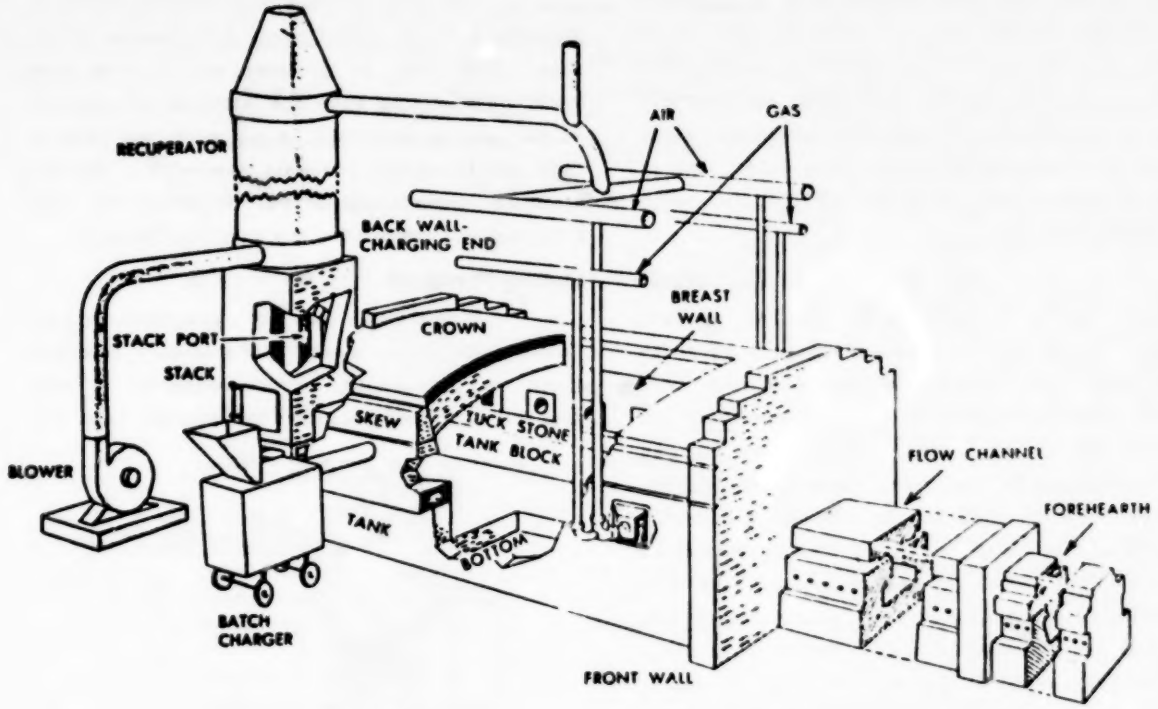


Fig. 3 - Recuperative fired furnace (4).

Fiberization

There are two major fiberizing methods for mineral wool production: blowing and centrifugal spinning. Long glass fibres may also be formed by drawing a filament from a glass melt. Regarding fibre quality and production rate, the centrifugal spinning process appears to occupy an intermediate position between the mechanical drawing and the blowing methods. For example, the drawing method produces fibres characterized by uniform diameter while the opposite occurs in the blowing process. Spun fibres occupy a mean position (2,5).

Blowing Method

A molten stream, tapped from the furnace, is subjected to a blast or jet of steam or high pressure air (Fig. 4). The impact breaks the melt into liquid globules which are propelled through the air. The air resistance during flight elongates the globules into fibres with a bead (waste shot) attaching to the end. The shot is less than 3 mm in diameter and cannot be recycled to the cupola. Thoenen suggests that shot was formed due to the premature cooling and solidification of the globule in its flight through the air (6). This could be remedied by manipulating the blowing operations to produce smaller globules and by increasing the steam pressure to raise the particle speed. Major variables affecting the fiberization are charge compositions, pouring rate, pouring temperature, molten stream temperature and thickness, height of drop of the melt stream before fiberization, type of nozzle, blowing medium and blowing pressure. Melt viscosity greatly influences the average fibre diameter of the blown wool. As viscosity increases, fibre diameter and shot size increase. An increase of temperature decreases viscosity. Both the higher temperature of melt and a shorter height of drop of the stream reduce the cooling of the melt. More shot is formed when the wool is blown at low temperatures. Shot formation rapidly increases as the amount of molten material delivered to the blowing jet exceeds the potential energy of the jet to convert the fused material to fibre (7). Zhilin states that

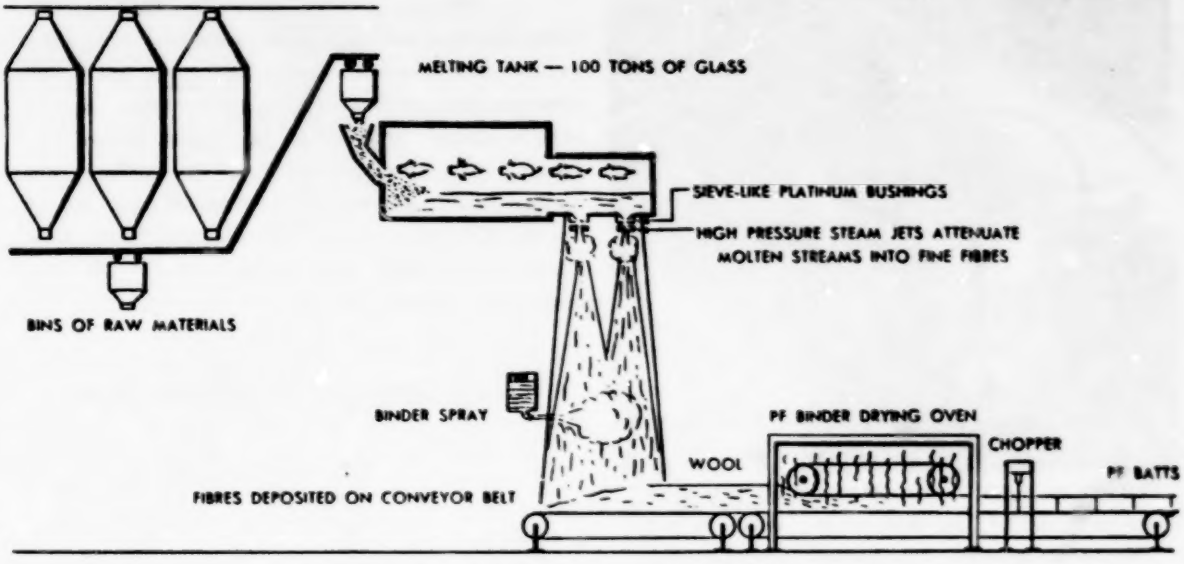


Fig. 4 - Steam blowing process (4).

the molten stream should not exceed 15 to 20 mm in thickness (8). Lowering the blowing pressure increases fibre diameter and shot content. The blowing pressure usually ranges from 310 to 862 kPa.

Centrifugal Spinning

There are variations of the spinning technique, employing disks, wheels or cups, and single or multiple configuration arrangements of spinners. All are, however, based on the centrifugal principle. The molten material is dispersed into fibres by the centrifugal force. In general, the diameter of spun wool depends chiefly on the rate of production, the fiberization temperature, the melt composition and viscosity. It is claimed that centrifugally spun wool contains less shot than that made by the blowing method (2). The spinning machines can be divided into three main groups:

(a) Figure 5 shows a typical example of the first group. The molten stream falls onto a rapidly rotating disk. The centrifugal force converts the melt into a fibrous mass. The fibres are driven into a box around the axle of the disk and then cut by knives (1) to a determined length and evacuated continuously by the action of the radial air jet from a circular nozzle (2).

(b) The second group employs a combination of several rotating wheels. The combination can be 3, 4 or 5 rotors. Figure 6 shows a 3-rotor arrangement (9). Rotor 1 is termed the distributor roll and rotors 2 and 3 are fiberizing rollers. Rotor 1 is so positioned and rotated to intercept the melt stream on a down-turning edge of its periphery. The stream is spread and accelerated by the distributor roll and discharged onto the fiberizing rotor 2 which is rotating in a direction opposite to that of rotor 1. A portion of the material is further discharged from rotor 2 to 3 which is rotating in the opposite direction to rotor 2. It is desired that no fibre be

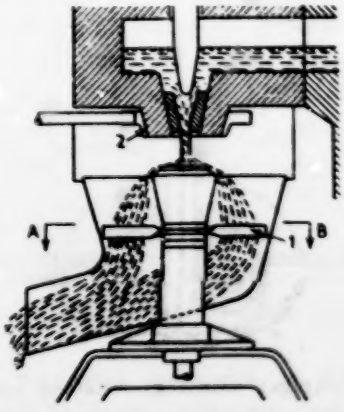


Fig. 5 - Centrifugal spinning, rotating disk (2).

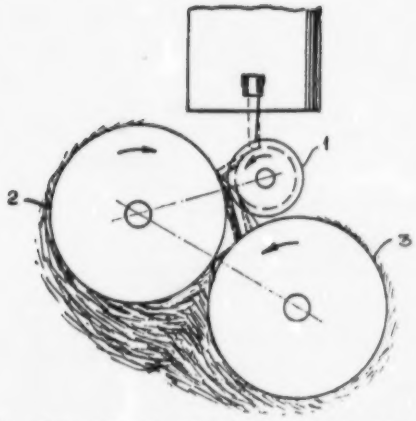


Fig. 6 - Centrifugal spinning, 3-rotor arrangement (9).

formed by rotor 1 and consequently little or no material of the melt stream should adhere to its periphery. The surface of this rotor is very smooth. On the other hand, it is essential for good fiberization that the material should bond to the peripheries of rotors 2 and 3. Small grooves or other textures are made on their surface. Rotor 1 may be rotated at a speed of 3000 to 4000 rpm, rotor 2 at 4000 to 5800 rpm and rotor 3 at 5000 to 6500 rpm. The speeds, the relative sizes, and the positions of the rotors can be varied to improve the production and quality of the mineral wool.

(c) The third group uses rotary containers. Figure 7 represents a typical example. The filaments of molten glass projected under the action of centrifugal force from the periphery of a rotating body (1) are subjected to the attenuating action of a blast of gaseous products obtained by combustion in the chamber (2) and projected through the slot (3).

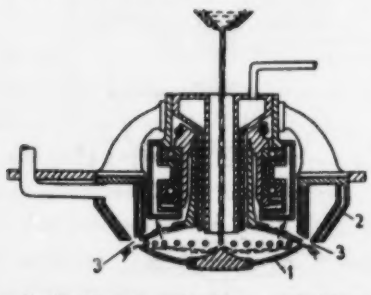


Fig. 7 - Centrifugal spinning, rotating container (2).

The Tel process, shown in Fig. 8, combines spinning and extrusion techniques (9). The melt stream is poured inside the rotor which has numerous fine perforations on its surface. A ring with a number of nozzles is placed around the rotor. The melt extruded through the perforations by the centrifugal force is subjected to a jet of hot gas from the nozzles and converted into long fibres by air resistance during flight. The shot content in this process is less than 1%.

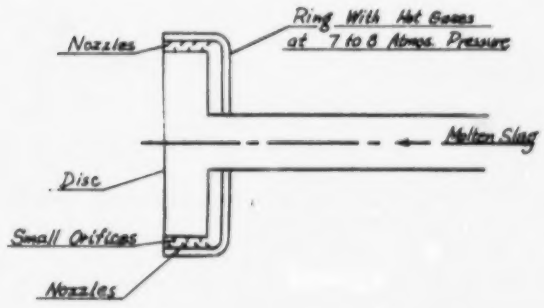


Fig. 8 - The Tel process (9).

Continuous Filament Process

The continuous fibre drawing method is shown in Fig. 9. Glass marbles are fed by gravity from a hopper into an electrically heated, platinum crucible having up to 200, 1-mm diam orifices in its bottom. The molten glass flows downward through the orifices. These fine streams of molten glass are gathered together and carried to a high speed winder. The molten glass streams can be attenuated by winding the filaments at a speed considerably faster than the stream flowrate from the melting crucibles. Some producers have melted glass directly in a larger furnace without the intermediate step of making marbles. Commercial alkali-resistant fibres are mostly made by the continuous filament process.

Properties of Glass Fibres

The strength of glass fibres depends on both the glass composition and the method of fibre production. High alkali content generally decreases fibre strength, particularly under wet conditions, and increases susceptibility to water attack. Water leaches alkali from the glass, leaving a siliceous skeleton which shows a reduced

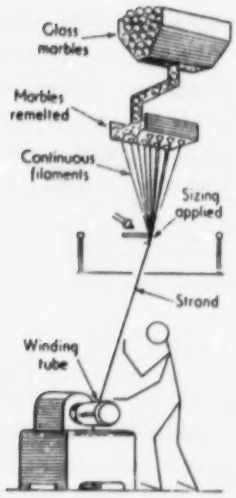
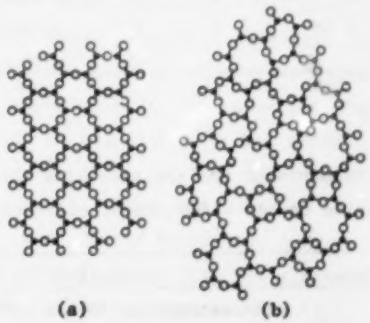


Fig. 9 - The continuous filament process (2,10).

strength. It is generally accepted that the rate of cooling and not the fineness of the fibre is the dominant factor affecting strength (11). When a glass fibre is formed, the glass is violently shock cooled. The time lapse, from the liquid glass to solid state in filament form cooled to room temperature, may be less than 0.01 s. The shock-cooled glass retains a frozen-in structure which is approximately that of the molten state. The structure is more uniform and perfect than that of the bulk glass, because flaw formation is greatly decreased. This results in much higher strength and lower density and modulus. Flexibility depends mainly on fibre diameter. The smaller the diameter, the greater the fibre flexibility. Glass fibres are non-cellular and tend not to absorb moisture. Surface moisture is less than 0.5% (2). Ordinary glass fibres are inert to oils, organic solvents and most acids but not to alkaline solutions. Glass fibres are also very resistant to mildew, moths, bacteria and rotting.

FUNDAMENTAL CONSIDERATIONS OF GLASS AND GLASS FIBRE

Mineralogically, mineral wool is formed as a glass in fibrous form on cooling from a silicate melt. The basic building block in silica based glasses is the $(SiO_4)^{-4}$ tetrahedron. Each Si^{+4} is coordinated by four O^{-2} ions. The tetrahedral coordination satisfies both the bonding requirements of covalent directionality and the relative size ratio (12). Because of the high charge on the Si^{+4} ion and its low ligancy or coordination number, the tetrahedra $(SiO_4)^{-4}$ are joined corner to corner to form an extended three-dimensional network with certain discontinuities. These discontinuities take the form of singly bonded oxygen atoms, each bearing a negative charge. To achieve electrical neutrality, cations such as Na^{+} and Ca^{+2} are situated adjacent to those discontinuities. The glass network, however, lacks the long-range order of crystals and the lattice is distorted. Figure 10 shows the structure difference between crystal and glass.

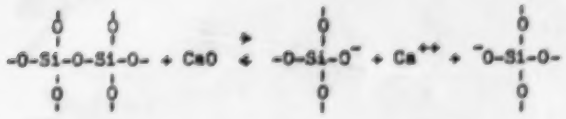


(a) (b)

Fig. 10 - Schematic representation of (a) crystalline lattice and (b) corresponding glassy network (13).

The oxide components in glass can be classified as basic, amphoteric and acidic as

shown in Table 4. When a basic oxide such as CaO is added to silica it will introduce O^{-2} ions into and break the Si-O network:



The number of broken joints depends on the ratio O/Si as indicated in Table 5.

Table 4 - Types of bonding and character of the oxides (13)

Oxide	Ionic fraction of bond	Coordination number solid-liquid		Character of the oxide
Na_2O	0.65	6	6 to 8	Network breakers or basic oxides
BaO	0.65	8	8 to 12	
SrO	0.61	8		
CaO	0.61	6		
MnO	0.47	6	6 to 8	
FeO	0.38	6	6	
ZnO	0.44	6		
MgO	0.54	6		
BeO	0.44	4		
Cr_2O_3	0.41	4		Amphoteric oxides
Fe_2O_3	0.36	4		
Al_2O_3	0.44	6	4 to 6	
TiO_2	0.41	4		
SiO_2	0.36	4	4	Network formers or acid oxides
P_2O_5	0.28	4	4	

Table 5 - Influence of the addition of a basic oxide on the structure of silicates (13)

O/Si	Formula	Structure
2/1	SiO_2	The tetrahedra form a perfect hexagonal network
5/2	$MO.2SiO_2$	One vertex joint breaks
3/1	$MO.SiO_2$	Two vertex joints are broken
7/2	$3MO.2SiO_2$	Three vertex joints are broken
4/1	$2MO.SiO_2$	Four vertex joints are broken

A direct result of this network-breaking action is the decrease of the softening and fusion temperatures of the glass. Another result is the viscosity decrease of the molten glass. Glass melt viscosity is a function of chemical composition and temperature. An increase in temperature causes progressive loosening of the silicate network structure by thermal agitation. This action will decrease viscosity according to:

$$\eta = A \exp(E_\eta / RT)$$

where A is a constant and E_η is the activation energy of viscous flow of the melt which depends on its composition. The addition of a basic oxide breaks the bonds between the $(SiO_4)^{-4}$ tetrahedra causing a decrease in the size of the silicate anions and consequently the activation energy and the melt viscosity (13).

Chemical Attack of Glasses in Aqueous Solutions

Glass can be chemically attacked by water and aqueous solutions of acids, alkalis and salts. Budd postulated two general types of chemical attack on silicate glasses: electrophilic and nucleophilic (14). Attacking reagents are classified into two groups - electrophilic reagents which always seek to attack positions where there is an excess of electrons, and nucleophilic reagents which always seek to attack positions where there is an electron deficit:

(a) Electrophilic attack may take place at negatively charged non-bridging oxygen atoms by electrophilic reagents H^+(or H_3O^+) and HCl and H_2SO_4 in the vapour phase (Fig. 11).

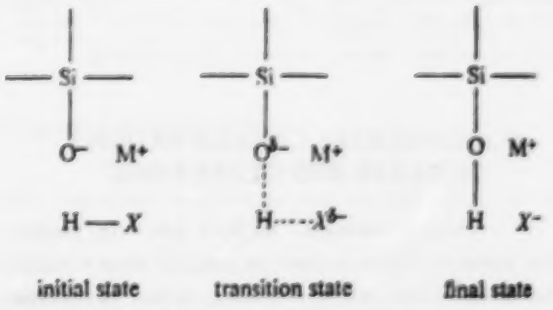


Fig. 11 - Electrophilic attack on non-bridging oxygen atom (14).

(b) Nucleophilic attack may take place at network silicon atoms by nucleophilic reagents O^{-2} and OH^{-}. The water molecule itself can act as a weak nucleophilic agent by virtue of the partial negative charge carried by the oxygen atom (Fig. 12).

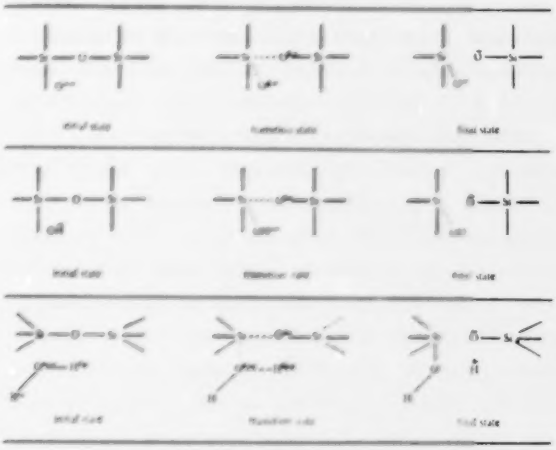


Fig. 12 - Nucleophilic attack on network silicon atom by (a) oxide ion (b) hydroxyl ion (c) water molecule (14).

El-Shamy et al investigated the reactions of glasses with aqueous solution and the effects of solution pH and glass composition (15). They found that there is a complicated physiochemical reaction between water and silicate glasses, not a simple dissolution of glass into water. The reaction comprises several individual processes such as hydration, dealkalization, and depolymerization, which occur simultaneously and influence one another to varying degrees. When a soda-silica or a soda-lime-silica glass is placed in water, changes occur in the glass and the solution. Two main reactions take place in the glass: extraction of alkali ions, with replacement by protons from the solution, and dissolution of silica by breakdown of the siloxane bonds at the interface between the solution and the attacked glass. The removal of silica usually lags behind the alkali extraction, thus leading to the formation of a silica-rich leached layer on the surface of the glass. This layer reduces the rate of alkali extraction by forming a barrier through which further alkali ions must diffuse before they can be extracted into solution. On the other hand, the water in contact with the glass changes very rapidly into a solution of alkali and silica. The pH of the solution, in turn, depends on the concentration and the relative ratio of alkali to silica. Both the concentration and ratio change with time therefore the pH of the solution is also expected to change accordingly.

The various factors affecting glass corrosion kinetics can be divided into two groups - sample states and corrosion conditions (16). Sample states include glass composition, mole fraction of a crystal phase, internal or applied stresses, surface roughness, phase separation, homogeneity and the form of the material, e.g., powder or bulk. Corrosion conditions include ranges of relative humidity, sulphur dioxide and other gas phase surface reactants, pH, the starting and final compositions of corrosion solutions, pressure and temperature of leaching, and the ratio of the solution volume to the surface area exposed.

Attempts have been made to study the influences of glass compositions and the addition of different oxides on the chemical durability of silicate glasses. A systematic substitution of TiO_2, GeO_2, ZrO_2 and $AlPO_4$ was made for silica in a soda-lime glass (17). Results showed substantial improvement in water and alkali resistance with ZrO_2. There was either no change or some deterioration of resistance with GeO_2. TiO_2 generally improved durability. $AlPO_4$ improved water and alkali resistance, but the acid attack was much increased. Equimolar substitution of Al_2O_3 for Fe_2O_3 in a silicate glass was found to reduce silica extraction in the alkaline region (18). This might be due either to the greater passivity of hydrated Al_2O_3 in the alkaline region or to SiO_2 having a lower activity in the Al_2O_3-SiO_2 system than in the Fe_2O_3-SiO_2 system. Less soda was extracted at pH ≥ 4 from the glasses containing Al_2O_3 than from those containing Fe_2O_3. Above pH 3 hydrated Al_2O_3 is stable and is well known to chemisorb sodium ions. Hydrated iron oxides are also capable of chemisorbing sodium ions, but less effectively. Chemical durability of some silicate glasses containing CaO, FeO and MnO was investigated (1). Molar substitution of FeO, and partic-

ularly of MnO for CaO in all these glasses increased the durability at pH 9 to 12. However, durability at pH 0 to 2 was found to deteriorate when this substitution was made. The acid and alkaline durability was satisfactorily correlated to the thermodynamic stability of the different oxides. The durability decreased with increasing soda content.

ALKALI-RESISTANT FIBRES

A variety of alkali-resistant fibres which cover a wide range of mineral compositions have been developed since the late 1960's when Building Research Station (BRS) in the UK pioneered research in making alkali-resistant fibres. A zirconia-containing fibre was produced by a simple glass-fibre drawing apparatus at BRS (19). The apparatus used a platinum crucible having a small orifice (2-3 mm diam) at the bottom to hold the glass melt. A glass thread was drawn through the orifice and attached to a winding drum to form fibre. The glass contained 71% SiO_2, 1% Al_2O_3 and 16% ZrO_2. The average reduction in diameter of this fibre in saturated $Ca(OH)_2$ solution at 100°C after 4 h is <1% compared with 10% for A-glass and 9% for E-glass (20). Paul calculated the thermodynamic stability of ZrO_2 in aqueous solution and found the hydrated ZrO_2 surface formed on the fibre was stable at all conceivable pH ranges and probably offered a very high activation barrier for diffusion of other ionic species through it (21). The pioneering research at BRS led to the commercial development of Cem-Fil glass fibre by Pilkington Brothers Ltd. Similar fibres have also been produced in the USA by Owens-Corning Fiberglass Corporation. The long-term durability of cement composites incorporating these fibres is being investigated in several countries (22).

An alkali-resistant fibre was produced based on a glass composition of an E-glass modified by adding zirconia or zirconia and titania (23). The preferred proportion of titania is from 1 to 6% by weight of the total glass composition, and that of zirconia from 2 to 6%. The total addition of zirconia and titania preferably should not exceed 8%. Examples of fibres having the following compositions by weight are: SiO_2 48.7%, Al_2O_3 13.25%; CaO 15.5%; MgO 4.8%; B_2O_3 9.75%; TiO_2 4%; and ZrO_2 4%. The glass was drawn from the melt at 1210°C into fibres, which exhibited a tensile strength of 0.91 GPa. After treatment in boiling saturated calcium hydroxide, the fibres retained about 65% of the original strength compared with 35% for the unmodified E-glass fibres.

A Japanese process provides alkali-resistant glass fibres having not more than 5% solubility in 10% NaOH at 100°C for 1 h, and not less than 80% of strength-retaining percentage (24). The fibres consist of: (mol %) SiO_2 56-76, ZrO_2 8-16; R_2O 1.5-25; P_2O_5 0.1-3; B_2O_3 0.5-7; R'O 0-10; SnO_2 0-7.5; other metal oxides 0-10; and CaF_2 0-2, where R is Li, Na or K, R' is Ca, Mg, Sr, Ba, Be, Zn or Pb, and other metal oxides are Al_2O_3, Fe_2O_3, TiO_2 or CeO_2. Ca ion in the cement paste is found to bond with P_2O_5 in the glass fibre to form a thin film of water and alkaline insoluble calcium phosphate on the surface of the glass fibre. This thin film acts as a protective film against alkaline solution. In addition, the presence of the thin film serves to improve the adhesion between the glass fibres and the cement matrix. However, when the concentration of P_2O_5 exceeds 3 mol %, the alkali resistance of the glass fibre is considerably deteriorated. ZrO_2 is effective in alkali resistance but its addition is limited to 11 mol % to obtain glass forming ability and stable melt spinnability. However, if both P_2O_5 and B_2O_3 are used, ZrO_2 can be added in amounts exceeding 11 mol % and up to 16 mol %, still with a good spinnability.

Corning Glass Works in the US has made a glass fibre from a batch comprising, by weight, from 85 to 99% basalt and from 1 to 15% ZrO_2 (25). Better chemical durability may be achieved where a basalt of low alkali metal oxide (<5%) is used. The addition of ZrO_2 to the basalt causes a phase separation when the melt is cooled. Although the exact function of the phase separation is not fully understood, it is believed that its presence is responsible for the greatly improved chemical durability. An increased ZrO_2 content will certainly further improve alkali resistance but in considering cost and increasing difficulty in melting and forming, the addition of more than 15% ZrO_2 is impractical.

In Germany, calcium silicate fibres have been made from phosphorus slag by adding 0.1 to 1% of at least one modifying oxide selected from zinc oxide, zirconium oxide, chromium oxide and titanium oxide (26). The fibres are suitable for use in cement-based building materials. Fibres containing 2-5 wt % zinc oxide and having a composition in wt % of 15-50 CaO, 40-65 SiO_2, and 1-20 Al_2O_3 are especially resistant to the alkaline environment of concrete.

A Swedish method produces alkali-resistant fibres by melting olivine alone or a mixture of olivine with clay minerals such as chamotte and possibly other minerals such as dolomite, quartz sand and sandstone (27). The clay minerals used should contain no more than 40 wt % of Al_2O_3, preferably less than 35%. Good alkali-resistant fibres can be produced having the following compositions:

	wt %
SiO_2	42-48
Al_2O_3	10-15
CaO	4-6
MgO	30-35
Iron oxides	2-4
Alkali metal oxides max.	1
Other oxides max.	1

One such mineral wool was produced by melting a mixture of 60% olivine-30% chamotte-10% dolomite. After soaking for 3 h at 100°C in a solution comprising 2 parts by weight NaOH and 1 part Na_2CO_3, the wool had a weight loss of 2.2% compared with 42.5% for a commercial glass wool.

Experiments were conducted at the University of California, Los Angeles, to determine the feasibility of using mixtures of waste slate and limestone to produce glass fibres as a substitute for asbestos (28,29). The alkali resistance of the fibres is superior to that of zirconia-containing glass fibres. Fibres made from an approximately equal mixture of slate and limestone give the best alkali resistance. The other advantages claimed are low cost, ready availability of raw materials, low melting point, and ease of rendering into glass fibres.

Alkali-Resistance Tests

Paul observed that there is no absolute or explicit measure for the chemical durability or resistance of a glass towards attack by aqueous solutions (21). Glasses are usually graded relative to one another after undergoing similar experimental conditions. Tests can be performed on carefully prepared graded glass grains or on a finished product; in this case on the produced fibres. The choice would normally depend on whether information is required on the intrinsic durability of a certain composition or on how the finished product will stand up to attack. Factors affecting chemical durability measurements of glasses are (a) weight of glass sample and surface area exposed, (b) ratio of the glass weight to the leaching solution volume, (c) nature of the leaching solution and frequency of replenishing it, and (d) temperature of leaching.

In general, a weighed amount of graded glass grains or glass fibres is put in a definite volume of a leaching solution and digested at a controlled temperature for a certain period. The digestion is usually carried out at elevated temperatures to accelerate leaching reactions. The weight loss of the sample and/or the solubilities of the different glass component oxides in the leaching solution are measured to determine the chemical durability. Various leaching solutions are used which include 5% NaOH (pH 12.0), 10% NaOH, a solution of 260 g $Na_4P_2O_7.10H_2O$ in 4.94 L distilled water, buffer solutions of saturated boric acid solution at 25°C + KOH solution (pH 9-12), saturated $Ca(OH)_2$ solution, a solution of 2 parts NaOH and 1 part Na_2CO_3 by weight, and cement extract solution (1,23,27-28,30-32). The saturated $Ca(OH)_2$ solution is believed to correlate reasonably well with the actual water plus cement mixture found in the cementitious mass (25). Cement extract solution is prepared by adding 500 g to 2.5 L distilled water in a polyethylene container. The container is inserted in a drum which is rolled at 19 rpm continuously for 16 d. The mix is filtered to obtain a clear solution having pH ~13 (32).

The resistance of glass fibres to alkali attack can also be measured by the reduction in

diameter and strength after alkaline leaching treatment. The diameters are measured by optical microscope using a Watson image-shearing eyepiece, a scanning electron microscope and an interference fringe technique (33). A scanning electron microscope can also be used to directly observe the surface of the corroded glass fibre (34). The strength of the fibres after alkaline treatment is frequently so low that they cannot be measured easily using a standard tensile testing machine such as Instron. A simple apparatus based on a double-pan analytical balance was designed for this measurement (33).

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